System for categorizing soil redox status by chemical field testing

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Abstract

Useful interpretation of the mixed redox electrode potentials measured in soils and natural waters in partial equilibrium with atmospheric O₂, is nearly impossible because most oxidized species of critically important N, S, Mn, Fe, and C are not electroactive. We propose that simple chemical tests be used in the field to group soils into the following soil redox status categories: Superoxic, Manoxic, Suboxic, Redoxic, Anoxic, and Sulfidic. These names connote status of oxidation and also indicate electron lability levels, respectively, of Very Low, Low, Medium, Medium High, High, and Very High. Tests involve qualitative measurement of tetramethylbenzidine oxidation colors, oxidation of added Cr, reduced Fe, easily reducible Fe, sulfide and other odors, and indicator pH.

1. Needed, a new system

Thermodynamic equilibrium is never reached in soils. Thus, the thermodynamic parameter, the redox potential, Eh or pe, is of no value in placing a field soil into a classification category. Because of the heterogeneity and instability of a non-equilibrium aerated soil system, an Eh or pe, measured either in the lab or in the field, is a confusingly mixed potential and is nearly useless. Furthermore, since the oxidized species of N, S, Mn, Fe, C, and H, major components of all partially oxidized soils, are not electroactive, they will not affect measured potentials. Exclusion of these species means that measured potentials are confusing at best and worthless at worst. Meaningful interpretation, thermodynamic or otherwise is not possible, using electrode potentials measured in partially oxidized soil systems (Bartlett, 1986; Bartlett and James, 1993).

2. The redox status categories

We propose a kinetically directed, qualitative, non-thermodynamic, empirical, and practical field oriented scheme for classifying soils according to redox status. Soils appear
naturally to be separated into six categories of soil redox status, according to redox behavior in the field. Each category represents a level of electron reactivity embodying a range of availabilities of electrons involved in soil redox. Along with the descriptive category name, the commonly used kinetic term, *lability*, also is useful for describing electron availability and reactivity. The *eL*, or electron lability level might be considered the kinetic analog of *pe*, the thermodynamic electron potential. However, *pe* (calculated from *Eh*) is theoretical and cannot be measured, even approximately, in a partially aerated soil. In contrast, an *eL* is empirical and practical and amenable to qualitative estimation in all soils. A designated *eL* level may range from *very low* to *very high* in serving to indicate the class level of soil redox behavior. It is not a thermodynamic parameter.

Proposed field chemical measurements provide a general framework that can be tied in with observations of redoximorphic features, botanical composition, and moisture and temperature regimes to contribute to and support the redox classification of field soils by category name. Following are the proposed redox categories, named according to redox status and also designated by a general electron lability (*el*) rating.

2.1. Superoxic

*Very low* *eL*

These soils are very highly oxidizing and contain highly available oxidants, especially Mn-oxides and Mn$_3^+$ or O free radicals. The O free radicals may be formed photochemically in oxygenated water interfacing with partially reduced soil solids. Also, certain dark colored A horizons developed from calcareous rock very high in Mn and Fe are powerful oxidizing soils, usually *Superoxic*.

2.2. Manoxic

*Low* *eL*

These are highly oxidizing soil systems that are well drained, contain mature humus, are mineralizing and nitrifying when moist, and are free of gleys mottles throughout the profile. Examples are tall corn or alfalfa soils, beech–maple climax forests, fertile A horizon material, and perhaps the garden of Eden.

2.3. Suboxic

*Medium* *eL*

These soils are oxidized and have nitrates present, but they also have significant potentials for reduction. Reducing tendency is balanced against oxidizing propensity. *Manoxic* soils often are temporarily *Suboxic* when electron availability is increased by drying, by additions of easily oxidized organic residues, by heavy rain during a warm season, or by compaction. Most dried and stored soil samples ("lab dirt") are *Suboxic*, as are organic horizons in well or moderately well drained forest soils, well cured composts and recently manured well or moderately well drained soils.
2.4. Redoxic

Medium high $eL$

Reducing and oxidizing tendencies are balanced somewhat in favor of reduction in these soils. Fe(II) is absent, except in very acid materials, and Fe(III) is found in recently oxidized forms that are easily reduced by the dipyridyl test in the light. The pH is lower than in related Anoxic soils, and some nitrate may be present. Hydric soils during cold or dry seasons, those artificially drained, or those heavily fertilized with nitrates, generally will be found to be Redoxic. Dried samples of Hydric soils will usually test Redoxic.

2.5. Anoxic

High $eL$

Presence of ferrous Fe is diagnostic for these strongly reducing and highly reduced soils wetland soils. Nitrates as well as pungent odors of decomposition tend to be absent, and pH's are usually near neutral. Newly flooded rice paddies and beaver ponds are examples.

2.6. Sulfidic

Very high $eL$

Sulfidic soils are very strongly reducing and are recognized by distinct and pervasive odors of vegetative putrefaction, especially of sulfides. Oxygen is absent; CH$_4$ and H$_2$S are produced; pH is near neutral. Sulfidic horizons, garbage landfills, manure lagoons, septic leachfields, and pond sediments are prime examples.

3. Field test chemical procedures

3.1. Tetramethylbenzidine oxidation

Slightly more than saturate a soil sample on a spotplate with TMB reagent [1.0 M acetic acid solution that is 10 mM MnSO$_4$, 10 mM K$_3$-citrate, and 1.0 mM 3,3',5,5'-tetramethyl-benzidine, an apparently safe substitute for carcinogenic benzidine (Liem et al., 1979)]. If out-of-doors or in in bright light, cover the spotplate loosely with a piece of black plastic to shut out excessive light.

A blue color around the edges of the spotplate spot after 20 to 30 min. indicates a one electron oxidation of TMB, usually by Mn oxides. Yellow color indicates a two-step electron oxidation. Development of yellow color, sometimes following blue and then green, is the result of of a two-step electron oxidation, and if it develops before 20 or 30 min., it is diagnostic for the Superoxic category. It is the probable indicator of the supermanganese Mn$^{3+}$ free radical (Liem et al., 1979; McBride, 1985; Bartlett and James, 1993). On addition of a few additional drops of TMB, a pale yellow color will turn into an intense blue color if the initial yellow was indicative of the two-step oxidation. However, if the quantity of TMB was excessive in the first place, it will not be oxidized beyond the blue color. The TMB concentration in the testing solution has shown that blue color, without initial yellow,
indicates a one electron oxidation of TMB, usually by reactive Mn-oxides or soluble Fe hydroxides.

In the procedure outlined here, yellow color around the edge of the soil spot indicates a very highly oxidized or Superoxic soil sample. Blue color, persisting for 30 minutes, identifies a highly oxidized or Manoxic soil. If Mn oxides are crystalline or otherwise low in reactivity, the blue color remains pale, and the color develops slowly. The boundary between Superoxic and Manoxic is somewhat arbitrary when based only on the TMB test.

The citrate concentration is high enough to prevent TMB blue color formation from Fe but low enough to allow a limited amount of reverse dismutation of highly reactive Mn(IV) oxides to form superoxidizing Mn(III) (Bartlett, 1988). Extremely acid soils often are depleted in Mn and if so, they will not exhibit positive TMB tests even when they are well aerated and highly aerobic.

### 3.2. Chromium oxidation

The test is performed in the field by adding 5 ml distilled H₂O and 0.1 ml (2 drops from a glass dropper) of 0.1 M CrCl₃ and 1 drop of 1 M HCl to approximately 0.5 cm³ (packed volume) of field moist soil in a 50 ml plastic beaker. After swirling intermittently for 15 min., add 1 drop of Cynamid 16 Superfloc solution [200 mg l⁻¹], mix, and allow to settle. Pour supernatant into a 4 ml test tube to a 3 ml mark, add 10 drops of DPC reagent mix, and observe the slow development of the magenta color, positive for Cr(VI). Rate the intensity of the magenta color as Positive + +, > 1 mg l⁻¹; Positive +, 0.1 to 1.0 mg l⁻¹; or positive −, barely visually detectable. [Prepare the DPC reagent by adding 60 ml of 85% phosphoric acid, diluted with 140 ml distilled H₂O, to 0.19 g of s-diphenylcarbazide dissolved in 50 ml 95% ethanol. Cr(VI) standards prepared in the lab will maintain their developed color in stoppered test tubes for several days; although, after some experience is gained, standards will become unnecessary for estimating the Cr(VI) result.]

A strong positive Cr(VI) net test is diagnostic for both Superoxic and Manoxic materials. In this test, added Cr(III) is oxidized by soil Mn-oxides to Cr(VI). It is termed a net test because only a part of the Cr(VI) formed is measured. Some Cr(VI) is reduced during the test by easily oxidizable organics (Bartlett and James, 1979; Bartlett, 1981). Such organics are prominent in Suboxic soils, and their effects in preventing net positive Cr(VI) from being expressed in these soils is enhanced by the acidification with HCl.

### 3.3. Ferrous iron test

Add 5 drops of 2,2'-dipyridyl (DIPY) reagent [10 mM reagent in pH 4.8 NH₄OAc, 1.25 M acetate] to a soil sample on a spotplate and note the color in the solution around the edges of the spot immediate pink at low light. Pink indicates ferrous Fe and is diagnostic for soil material that is highly reduced (Anoxic) or very highly reduced (Sulfidic).

### 3.4. Easily reducible iron

Add enough 0.1 M Oxalic acid to saturate a pinch of field moist soil on a spotplate and place in bright light [sunlight or artificial] for 5 min. or bright shade 30 min. or deep shade.
for up to an hour. After the light exposure, add 5 drops of DIPY reagent and note absence or presence of pink or red color. A positive test for Fe(II) after oxalate and light identifies easily reducible Fe(III) such as is found in a *Hydric Soil* during a dry season. It is diagnostic for the *Redoxic* category. The test combines extraction of reactive Fe(III) by the organic acid and its reduction to Fe(II) by the organic/light interaction (Childs, 1981; Bartlett and James, 1993; McMahon, 1967). The dipyridyl is a stronger reductant than either oxalate or citrate. Oxalate is a stronger reductant than citrate, but citrate is a much stronger complexing agent and extractant for Fe than is oxalate. If DIPY is added in the presence of light or if DIPY and citrate are used in combination, too much difficult-to-reduce Fe(III) is included and soils that are lower *el* soils than *Redoxic* will end up with positive tests for easily reducible Fe. Oxalate, with moderate Fe reducing and extracting power seems to be quite satisfactory. Dipyridyl acts only as an indicator for Fe(II).

### 3.5. Common scents

Detection entails sniffing, without addition of acid, of odoriferous emanations from wet soil reminful of anaerobic decomposition. In addition to these common scents, the characteristic and distinctive *rotten egg odor* of H₂S evolution upon addition of 1 M HCl must also be present if a soil is to be classified *Sulfidic*. The familiar anaerobic scents that disappear when sulfidic material is dried and oxidized are more important in diagnosing the *Sulfidic* redox category than is the H₂S release with acid since sulfidic material recently dried and partially oxidized, so that it no longer belongs in the *Sulfidic* category, may still release H₂S on acidification.

### 3.6. *pH* with Vermont indicator

To prepare indicator, dissolve in 185 ml 95% ethanol, 110 mg of brom cresol green, 75 mg brom cresol purple, 25 mg methyl red, 50 mg methyl orange, and 23 mg phenolphthalein, add 10 mM CaCl₂ and about 980 ml distilled water. Stir until all residues are dissolved, adjust pH to 5.8 with 0.10 M NaOH, and bring to 1 l final volume.

The following colors will be observed when the indicator is added to pH buffers: pH 3, light reddish orange; pH 4, darkish orange (slightly brownish); pH 5, olive brown; pH 6, green; pH 7, greenish blue; pH 8, bluish purple.

In the field, add indicator to a pinch of moist soil in a spotplate so that the solution volume is in slight excess. After mixing, quickly read the color around the edges as the soil settles. Because soils may adsorb dyes individually, colors seen vary from those in buffer solutions. Still, indicator pH is quite adequate for the separations needed in the present procedure. Because bright sunlight can decolorize dyes, comparing hue is better than brightness or intensity. Color charts are less satisfactory than standard buffer solutions. Although not always more accurate, a portable pocket pH meter could certainly be more convenient.
4. Using test results to place soils into redox categories

<table>
<thead>
<tr>
<th>Test results</th>
<th>Redox status classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A] + TMB yellow or green; pos. Cr(VI)</td>
<td>Superoxic</td>
</tr>
<tr>
<td>[B] + TMB blue; pos. Cr(VI)</td>
<td>Manoxic</td>
</tr>
<tr>
<td>[C] + TMB; pos. Cr(VI); pH &lt; 5.3 (greenish brown ind.)</td>
<td>Manoxic</td>
</tr>
<tr>
<td>[D] + TMB blue; neg. Cr(VI); pH &lt; 5.3</td>
<td>Suboxic</td>
</tr>
<tr>
<td>[E] + TMB blue; pos. Cr(VI); pH &gt; 5.3 (brownish green)</td>
<td>Suboxic</td>
</tr>
<tr>
<td>[F] + easily reducible Fe(III); + TMB; pos. + Cr(VI)</td>
<td>Redoxic / Manoxic</td>
</tr>
<tr>
<td>[G] + easily reducible Fe(III); neg. TMB; neg. Cr(VI)</td>
<td>Redoxic</td>
</tr>
<tr>
<td>[H] pos. Fe²⁺; + TMB and/or pos. Cr(VI) Fe²⁺; neg. or pos. H₂S w HCl; neg. TMB; neg. Cr(VI)</td>
<td>Manoxic / Anoxic</td>
</tr>
<tr>
<td>[J] pos. Fe²⁺; pos. H₂S w HCl; odoriferousness / o HCl</td>
<td>Sulfidic</td>
</tr>
</tbody>
</table>

Cr(VI) ratings: pos. = barely visually detectable. pos. + = estimated 0.1–1 mg l⁻¹. pos. 2+ = estimated > 1 mg l⁻¹. +TMB = faint to strong blue. + TMB blue = clearly blue.

4.1. Manganese, the key

Soil Mn, or its lack, appears to be the key to the entire spectrum of soil redox behavior and status. Except for the sniff tests, decisions can be made about all six categories of soil redox status using only TMB and the Cr oxidation tests, both of which identify oxidized forms of Mn.

4.2. Double categories

Any soil sample, as a non-equilibrium redox system, is made up of a mixture of redox states. Generally, contrasting states tend to cancel the effects of one another because they exist in some sort of metastable equilibrium with an easily detectable predominating redox status. However, an occasional single soil sample can be shown by chemical tests to contain two or more discreet and contrasting redox status portions. In E above, ferrous Fe and reactive Mn oxides are present together. Such a sample requires a double redox status name. In a double named category, the dominant redox category name is second, with the first becoming the modifier. Whenever the Cr(VI) test is positive, Manoxic [or Superoxic] will be part of the status name, and whenever Fe²⁺ is positive, Anoxic will be part of the name. A soil testing positive for easily reduced Fe(III) would be Suboxic if it had a positive TMB test and Redoxic if TMB were negative.

4.3. Contrasting redox layers

When double-named categories include contrasting redox domains, the slash between two names will indicate a redox interface. In a classic flooded soil, it is common to find the
TMB test indicating *Superoxic* soil material on the aerated side of an interface that has an *Anoxic* soil containing ferrous Fe below it. A Pt electrode responding only to the solution phase would give an average value, weighted in favor of species that are both soluble and electroactive, generally those found only under anaerobic conditions.

4.4. Borderline soils

The pH is useful in deciding the redox classifications of soils that are truly borderline between adjoining redox categories. An acid soil, compared with a neutral soil, tends to be more oxidized than field tests might indicate. For example, a soil with a pH < 4 will oxidize Cr(III) only if it contains highly reactive Mn oxides or perhaps available free radicals; whereas a near neutral pH soil is more likely to contain reactive Mn oxides than an acid soil even if the total Mn supply is low. If a soil is borderline and the pH is < 5.3 (greenish brown Vermont indicator test), it should be placed in the category on the better oxidized side of the border, and, if the pH is > 5.3 (brownish green), it should be placed on the lesser oxidized side.

5. Variability of redox status

The distinctive features of a specific redox status category should be considered to refer only to the particular sample being tested at the point in time of testing. A redox species is transitory; a redox category designation is an intensity parameter. It will vary with time in minutes, hours or seasons. It will vary with location, from pedon to pedon, from horizon to horizon, ped to ped, inside of a ped to the outside of the ped. The sediments at the bottom of a pristine lake usually will be *Manoxic*; whereas a well drained "sanitary" landfill (not pristine) could be *Anoxic* or even *Sulfidic*. A well aerated soil may produce a negative, low, medium, or high Cr net test. The variations are real and not sampling errors. Manganese oxides, reducing organics, and even Fe$^{++}$ can exist side by side with less than a millimeter of interfacial boundary separating them. A Mn oxide coating can exist for long periods on the outside of a soil ped without oxidizing adsorbed Fe(II) inside. However, because the sample is thoroughly mixed during the test equilibration, the Cr net test will integrate the redox across such an interface and supply a compromise answer (Bartlett, 1981).

6. Chemical identification of hydric soils

The low eL categories of *Sulfidic, Anoxic, and Redoxic* soil materials, all are identifiable by simple chemical field tests as categories with characteristics of poorly or very poorly drained soils, that is, Hydric or wetland soils that develop wherever a water table is near or above the soil surface for a sufficient length of time during a season warm enough for reduction to take place.

By inducing changes in the availability of O$_2$, the ultimate electron acceptor, altering water table depths by natural or artificial drainage or flooding of a soil, can be expected to cause temporary or long lasting shifts in reducing tendency and reducing power and therefore
in Redox Status category. Sometimes, the simple presence of \( \text{Fe}^{2+} \) has been used to indicate hydric character. But reliance on such a test is misleading because of the ephemeral nature of ferrous Fe. A soil testing positive will be hydric only at the moment of testing. The \( \text{Fe}^{2+} \) is quickly oxidized as the soil is partially dried or drained. However, even though \( \text{Fe}^{2+} \) is absent, the soil may still be Hydric, according to other Hydric soil criteria. Redoximorphic features such as accumulation of organic matter and the presence of gley mottles, along with presence of hydrophytic vegetation provide some positive identification of hydric character, even when the soils are dry. The light induced Fe(II) positive test can provide strong reinforcement of this identification.

Drying an Anoxic soil, which most surely is also a Hydric soil, oxidizes the Fe(II) in it to Fe(III), converting it to a Redoxic soil, which is still Hydric, even though its Fe(II) has vanished. Thus the field test for easily reduced Fe(III), specific for Redoxic status, also serves to identify a Hydric soil that has been drained or dried. Any dry soil containing easily reduced Fe(III) probably contained Fe(II) when it was last wet. However in its present dry state, it may contain reactive Mn oxide by the TMB test, meaning that its present classification would be Suboxic. On wetting, the Mn oxides will disappear by reduction, and the soil will become Redoxic, as it would have been classified when dry, if Mn oxides had been absent. Probably a soil should be considered Hydric if it had ferrous Fe in its recent past, regardless of its present redox status. The DIPY test in the light makes this easily discernible.

References